

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau**D28**

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | |
|---|-----------|---|
| (51) International Patent Classification ⁷ : C08L 101/00, 21/00, 77/00, C08J 3/22, C08L 67/02 // (C08L 101/00, 91:00) (C08L 21/00, 91:00) | A1 | (11) International Publication Number: WO 00/64985 (43) International Publication Date: 2 November 2000 (02.11.00) |
| (21) International Application Number: PCT/NL00/00177 (22) International Filing Date: 17 March 2000 (17.03.00) (30) Priority Data: 1011896 27 April 1999 (27.04.99) NL (71) Applicant (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). (72) Inventor; and (75) Inventor/Applicant (for US only): WILLEMS, Edwin [NL/NL]; Rolandsweg 8, NL-6136 BV Sittard (NL). (74) Agent: DORRESTIJN, Antoon; DSM Patents & Trademarks, P.O. Box 9, NL-6160 MA Geleen (NL). | | (81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> |
| (54) Title: PREPARATION OF A THERMOPLASTIC ELASTOMER HAVING A LOW HARDNESS (57) Abstract Process for the preparation of a thermoplastic elastomer containing a thermoplastic polymer with polar groups, a rubber and an oil in which the thermoplastic polymer with polar groups is mixed with the rubber and the oil and in which the rubber is dynamically vulcanized. At least a part of the oil is added after the rubber has at least partly vulcanized. | | |

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | | | |
|----|--------------------------|----|--|----|--|----|--------------------------|
| AL | Albania | ES | Spain | LS | Lesotho | SI | Slovenia |
| AM | Armenia | FI | Finland | LT | Lithuania | SK | Slovakia |
| AT | Austria | FR | France | LU | Luxembourg | SN | Senegal |
| AU | Australia | GA | Gabon | LV | Latvia | SZ | Swaziland |
| AZ | Azerbaijan | GB | United Kingdom | MC | Monaco | TD | Chad |
| BA | Bosnia and Herzegovina | GE | Georgia | MD | Republic of Moldova | TG | Togo |
| BB | Barbados | GH | Ghana | MG | Madagascar | TJ | Tajikistan |
| BE | Belgium | GN | Guinea | MK | The former Yugoslav Republic of Macedonia | TM | Turkmenistan |
| BF | Burkina Faso | GR | Greece | ML | Mali | TR | Turkey |
| BG | Bulgaria | HU | Hungary | MN | Mongolia | TT | Trinidad and Tobago |
| BJ | Benin | IE | Ireland | MR | Mauritania | UA | Ukraine |
| BR | Brazil | IL | Israel | MW | Malawi | UG | Uganda |
| BY | Belarus | IS | Iceland | MX | Mexico | US | United States of America |
| CA | Canada | IT | Italy | NE | Niger | UZ | Uzbekistan |
| CF | Central African Republic | JP | Japan | NL | Netherlands | VN | Viet Nam |
| CG | Congo | KE | Kenya | NO | Norway | YU | Yugoslavia |
| CH | Switzerland | KG | Kyrgyzstan | NZ | New Zealand | ZW | Zimbabwe |
| CI | Côte d'Ivoire | KP | Democratic People's Republic of Korea | PL | Poland | | |
| CM | Cameroon | KR | Republic of Korea | PT | Portugal | | |
| CN | China | KZ | Kazakstan | RO | Romania | | |
| CU | Cuba | LC | Saint Lucia | RU | Russian Federation | | |
| CZ | Czech Republic | LI | Liechtenstein | SD | Sudan | | |
| DE | Germany | LK | Sri Lanka | SE | Sweden | | |
| DK | Denmark | LR | Liberia | SG | Singapore | | |
| EE | Estonia | | | | | | |

PREPARATION OF A THERMOPLASTIC ELASTOMER

5

HAVING A LOW HARDNESS

The invention relates to a process for the preparation of a thermoplastic elastomer containing a thermoplastic polymer with polar groups, a rubber and
10 an oil, in which process the thermoplastic polymer with polar groups is mixed with the rubber and the oil and the rubber is dynamically vulcanized.

Such thermoplastic elastomers with dynamically vulcanized rubber are described in the
15 "Handbook of Thermoplastic Elastomers, by B.M. Walker / C.P. Rader, chapter 4, Elastomeric Alloy Thermoplastic Vulcanisates Van Nostrand Reinhold, New York 1988".

When a rubber is vulcanized in the normal way, a product having the properties of a thermosetting
20 material is formed.

The thermoplastic elastomers with dynamically vulcanized rubber (hereinafter referred to as TPVs) contain vulcanized rubber, which is dispersed in the form of fine particles in a continuous phase of
25 a thermoplastic polymer.

TPVs are special in that they have a number of properties of the thermoplastic polymer that forms the continuous phase. Thus, TPVs can be processed as thermoplastics and use can be made of the customary
30 techniques for shaping and reprocessing.

To improve the elastic properties and processing properties of TPVs, an oil is often added to the composition.

A drawback of the use of oil in a TPV
35 containing a thermoplastic polymer with polar groups is

that TPVs are formed in which the vulcanized rubber is poorly dispersed. It is even possible for the continuous phase to be formed not by the thermoplastic with polar groups, but by the rubber, so that the
5 advantageous properties of the TPVs as a thermoplastic with respect to processability are lost.

The object of the present invention is to provide a process for the preparation of a thermoplastic elastomer containing a thermoplastic
10 polymer with polar groups, a rubber and an oil in which the rubber is dynamically vulcanized, that does not have said drawback.

This object is achieved in that at least a part of the oil is added after the rubber has at least
15 partly vulcanized.

Surprisingly, it has been found that when the process according to the present invention is used TPVs containing a thermoplastic polymer with polar groups, a rubber and an oil can be prepared with a good
20 dispersion of the vulcanized rubber.

A further advantage of the process according to the present invention is that the TPVs can even be prepared with high oil contents while the TPVs still have a good processability as thermoplastics.

25 Yet another advantage of the process according to the present invention is that the TPVs can be made that have a very low hardness and a good compression set.

As oil in the process according to the
30 present invention use can be made of paraffinic, naphthenic as well as aromatic oils or of mixtures of these oils.

The total quantity of oil that is present

in the TPV after the process according to the invention has been carried out ranges, for instance, from 0.05 to 2.5 times the quantity of rubber present in the TPV.

Preferably, the total quantity of rubber
5 amounts to between 0.1 and 1.6 times the quantity of rubber present in the TPV. With special preference the total quantity of oil amounts to between 0.5 and 1.2 times the quantity of rubber present in the TPV.

To prepare the TPVs with a good dispersion
10 of the vulcanized rubber and a good processability as a thermoplastic, all or part of the oil for the process according to the invention is added after the rubber has at least partly vulcanized.

Preferably, the quantity of oil that is
15 added after the rubber has at least partly vulcanized is between 50 and 100% of the total quantity of oil. Special preference is given to the process according to the invention, in which 100% of the oil is added after the rubber has at least partly vulcanized.

20 As thermoplastic polymer with polar groups in the TPVs of the invention use can be made of all known thermoplastic polymers with polar groups. Examples of thermoplastic polymers with polar groups that are suitable for use in the process according to
25 the present invention are: polyamides, polyesters, polyacrylates, polycarbonates and copolyether ester block polymers or mixtures of these polymers.

Preferably, a polyamide or a polyester is used as thermoplastic polymer with polar groups.
30 Examples of polyamides that can be used in the process according to the present invention are: polyamide 6, polyamide 4,6, polyamide 6,6 and polyamide 11. Examples of polyesters that can be used in the process

according to the present invention are: polyethylene terephthalate and polybutylene terephthalate.

Special preference in this invention is given to the use of copolyether ester block copolymers with polar groups as thermoplastic polymer with polar groups, or to the use of a mixture of a copolyether ester block copolymer and a polyester. With these, TPVs can be prepared that have a very low hardness and a good compression set. Examples of copolyether ester block copolymers that can be used in the process according to the invention are: copolybutylether butylene terephthalate block copolymer and copoly (1-methyl) ethylether butylene terephthalate block copolymer.

The quantity of the thermoplastic polymer with polar groups that is used in the process according to the invention ranges from 0.2 to 5.0 times the quantity of rubber present in the TPV. Preferably, the quantity of the thermoplastic polymer with polar groups ranges from 0.5 to 2.0 times the quantity of rubber present in the TPV.

In the preparation of TPVs according to the process of the invention many customary rubbers that are capable of dynamic vulcanization can be used as rubber.

Use can for instance be made of the following rubbers or a mixture thereof: SBR (styrene butadiene rubber, copolymer of styrene and butadiene), NBR (nitrile rubber, copolymer of butadiene and acrylonitrile), IIR (butyl rubber, copolymer of isobutene and isoprene) or BR (butadiene rubber). Other examples of rubbers that can be used in the process according to the invention are styrene containing block

copolymers such as for instance: SBS (styrene butadiene block copolymer), SEBS (styrene ethylene/butadiene styrene block copolymer), SIPS (styrene isoprene block copolymer). Yet other examples of rubbers that can be
5 used in the process according to the invention are a copolymer of ethylene, an α -olefin and a third monomer or a mixture with a copolymer of ethylene and an α -olefin. The α -olefin can for instance be propylene, in these cases the rubber is called EPDM and EPM.

10 Preferably, SBR, SBS, SEBS, SIPS, NBR, IIR, BR or a mixture of these rubbers is used as rubber in the process according to the invention.

In the process according to the invention most preferably use is made of EPDM rubber or a mixture
15 of EPDM and EPM rubber or a mixture of EPDM, EPM and one or more of the following rubbers: SBS, SEBS and SIPS.

The TPV prepared according to the process of the invention for instance contains 5 - 250 parts of
20 oil and 20 - 500 parts of thermoplastic polymer with polar groups per 100 parts of rubber. Preferably, the TPV according to the process of the invention contains 10 - 160 parts of oil and 50 - 200 parts of thermoplastic polymer with polar groups per
25 100 parts of rubber.

In addition, the TPV prepared according to the process of the invention can for instance contain additives. Examples of such additives are fillers, reinforcing agents, dyestuffs, stabilizers and
30 vulcanization agents.

Preferably the TPV prepared according to the process of the invention exists of the

thermoplastic polymer with polar groups, the rubber, the oil and the additives.

Furthermore in the TPV prepared according to the invention substances can for instance be present to increase the compatibility between the rubber and the thermoplastic polymer with polar groups used. Examples of these substances are maleic anhydride-modified, alkoxy silane-modified, epoxy-modified, acid-modified thermoplastic polymers and/or rubbers.

The dynamic vulcanization of the rubber used in the process according to the invention is carried out in the presence of a vulcanization agent, which is added to the mixture in a quantity known to one skilled in the art. As vulcanization agent in the dynamic vulcanization use can be made of the vulcanization agents that are known in literature. Preferably, a peroxide, a sulphur compound, a hydrosilane or a phenol resin is used as vulcanization agent.

At least part of the oil is added after the rubber has at least partly vulcanized. At the moment that the oil is added the quantity of vulcanized rubber is for instance between 50 - 100% of the total quantity of rubber present. Preferably, the rubber present is 100% vulcanized.

The extent to which the rubber is vulcanized at the moment that at least part of the oil is added is determined by measuring the quantity of soluble rubber in boiling xylene.

The extent to which the rubber is vulcanized is calculated using formula I:

$$\frac{A - B}{A} \times 100\% \quad (I)$$

- 5 where A: the total quantity of rubber
B: the quantity of rubber dissolved in boiling xylene.

The process according to the invention can take place using the equipment known from literature for mixing rubbers with thermoplastics and oil in
10 continuous and discontinuous processes.

Preferably, the equipment for the process according to the present invention is an extruder or a batch kneader.

The TPVs obtained by the use of the process
15 according to the invention are suitable for all kinds of applications in shaped articles made from thermoplastic elastomers containing a thermoplastic polymer with polar groups, a rubber and an oil.

In particular this relates to applications
20 of thermoplastic elastomers in which a low hardness and a good compression set over a wide temperature range are important.

By the choice of the thermoplastic elastomer with polar groups to be used, the rubber and
25 the oil and the quantities to be used of the substances, it is ensured that the TPV according to the invention has the material properties that are needed for the application.

The hardness of the TPV for this
30 application preferably amounts to between 20 Shore A and 40 Shore D. Special preference is given to a TPV of which the hardness amounts to between 30 and 70 Shore A.

Preferably, the compression set (ISO 815)

of the TPV for this application amounts to between 10 and 50%.

Preferably, the compression set (DIN 35517, B) of the TPV for this application amounts to between 10 and 70%.

The shaped articles of the applications are made using the customary processing methods such as for instance: extrusion, blow moulding and injection moulding.

The TPVs according to the invention can be used in applications for the automotive industry, for instance: door profiles, bellows, cable sheathings, hoses, air bag covers, dashboard films, handles and soft-touch applications.

15

Comparative experiment A

In a batch kneader a mixture of the following mass ratios is made:

100 parts of EPDM rubber (Keltan[®], supplied by DSM)
75 parts of copolyether ester (Arnitel[®] EM 400, supplied by DSM)
10 parts of white pigment (Kronos[®] 2210, supplied by Kronos)
1 part of stabilizer (Irganox[®] 1098, supplied by Ciba Geigy).

25

After heating to 205°C and mixing, 10 parts of phenol resin (SP 1045, supplied by Schenectady) are added and the dynamic vulcanization of the rubber starts.

30

This composition is mixed for 2 minutes at 205°C.

Examples I - VI

The following experiments were carried out, with 6 x a composition according to A being made in a batch kneader.

- 5 After mixing for 2 minutes at 205°C, a quantity of oil (Sunpar[®], supplied by Sun Oil) according to Table 1 is added, followed by another 5 minutes' mixing.

10 Table 1

| Comparative experiment / example | Quantity of oil (parts) | Material characterization |
|----------------------------------|-------------------------|---------------------------------|
| A | 0 | homogeneous melt, thermoplastic |
| I | 20 | homogeneous melt, thermoplastic |
| II | 40 | homogeneous melt, thermoplastic |
| III | 60 | homogeneous melt, thermoplastic |
| IV | 80 | homogeneous melt, thermoplastic |
| V | 100 | homogeneous melt, thermoplastic |
| VI | 120 | homogeneous melt, thermoplastic |

- After cooling of the thermoplastic elastomer, the hardness and the compression set are measured (see Table 3).
- 15

Comparative experiments B - G

The following six experiments were carried out, in which mixtures in the following mass ratios were made on a batch kneader:

100 parts of EPDM rubber (Keltan®)
75 parts of copolyether ester (Arnitel® EM 400)
10 parts of white pigment (Kronos® 2210)
1 part of stabilizer (Irganox® 1098).

The quantity of oil (Sunpar® 150) is added according to Table 2.

This composition is heated and mixed for 2 minutes at 230°C, then a quantity of 10 parts of phenol resin (SP 1045) is added, after which mixing is continued for 5 minutes. As soon as the phenol resin is added, the dynamic vulcanization of the rubber starts.

Table 2

| Comparative experiment | Quantity of oil (parts) | Material characterization |
|------------------------|-------------------------|---|
| B | 20 | homogeneous melt, thermoplastic |
| C | 40 | homogeneous melt, thermoplastic |
| D | 60 | crumbly material, no thermoplastic |
| E | 80 | crumbly material, no thermoplastic |
| F | 100 | very crumbly material, no thermoplastic |
| G | 120 | very crumbly material, no thermoplastic |

After cooling of the composition the hardness and the compression set are measured (see Table 3).

Table 3, test results

| Comparative experiment/ example | Hardness Shore A | Compression set % (ISO 815) | | | | Compression set (DIN 35517, B) | | | |
|---------------------------------------|---------------------|--------------------------------|---------------------|----------------------|---------------------|-----------------------------------|----------------------|--|--|
| | | 72 hrs. and 23°C | 24 hrs. and 70°C | 24 hrs. and 100°C | 24 hrs. and 23°C | 24 hrs. and 70°C | 24 hrs. and 100°C | | |
| A | 68 | 24 | 44 | 48 | 24 | 55 | 67 | | |
| I | 63 | 24 | 41 | 45 | 24 | 53 | 65 | | |
| II | 56 | 23 | 39 | 42 | 23 | 51 | 62 | | |
| III | 50 | 22 | 37 | 38 | 22 | 48 | 59 | | |
| IV | 43 | 20 | 35 | 39 | 20 | 47 | 56 | | |
| V | 38 | 21 | 34 | 35 | 21 | 44 | 55 | | |
| VI | 32 | 20 | 32 | 36 | 20 | 42 | 51 | | |
| B | 61 | 25 | 42 | 41 | 25 | 52 | 63 | | |
| C | 53 | 25 | 40 | 41 | 25 | 51 | 62 | | |
| D | 45 | 24 | 38 | 37 | 24 | 52 | 61 | | |
| E | 39 | 26 | 39 | 40 | 26 | 53 | 61 | | |
| F | 31 | 26 | 39 | 37 | 26 | 50 | 60 | | |
| G | 26 | 27 | 40 | 40 | 27 | 52 | 62 | | |

From examples I - VI it is clear that when the quantity of oil increases the thermoplastic elastomer made has a lower hardness and a better compression set in comparison with A. In these
5 thermoplastic elastomers the thermoplastic polymer that is present forms the continuous phase.

From comparative experiments B - G it is clear that B and C are still behaving as thermoplastics, but the compositions of experiments D -
10 G no longer behave as thermoplastics because the rubber forms the continuous phase. Furthermore compositions B - G, with increasing quantities of oil, do prove to have a lower hardness, but the compression set remains virtually unchanged.

CLAIMS

1. Process for the preparation of a thermoplastic elastomer containing a thermoplastic polymer with polar groups, a rubber and an oil, in which the thermoplastic polymer with polar groups is mixed with the rubber and the oil and in which the rubber is dynamically vulcanized, characterized in that at least part of the oil is added after the rubber has at least partly vulcanized.
2. Process according to claim 1, characterized in that the total quantity of oil in the thermoplastic elastomer is between 0.1 and 1.6 times the quantity of rubber present.
3. Process according to claim 1, characterized in that the total quantity of oil in the thermoplastic elastomer is between 0.5 and 1.2 times the quantity of rubber present.
4. Process according to claim 1, characterized in that between 50 and 100% of the oil is added after the rubber has at least partly vulcanized.
5. Process according to claim 1, characterized in that 100% of the quantity of oil is added after the rubber has at least partly vulcanized.
6. Process according to claim 1, characterized in that said thermoplastic polymer with polar groups is a polyamide, or a polyester, or a mixture of polyamide and a polyester.
7. Process according to claim 1, characterized in that said thermoplastic polymer with polar groups is a copolyether ester block copolymer, or is a mixture of a copolyether ester block copolymer and a polyester.

8. Process according to claim 1, characterized in that the rubber used is SBR, SBS, SEBS, SIPS, NBR, IIR, BR or a mixture of these rubbers.
9. Process according to claim 1, characterized in that the rubber is EPDM or a mixture of EPDM and EPM, or a mixture of EPDM, EPM and one or more of the following rubbers: SBS, SEBS and SIPS.
10. Process according to claim 1, characterized in that the quantity of thermoplastic polymer with polar groups in the thermoplastic elastomer is between 0.5 and 2.0 times the quantity of rubber present.
11. Thermoplastic elastomer obtainable by the process according to claims 1 - 10.
12. Shaped article containing a thermoplastic elastomer according to claim 11, characterized in that the hardness of said article is between 20 Shore A and 40 Shore D.
13. Shaped article containing a thermoplastic elastomer according to claim 11, characterized in that the hardness of said article is between 30 and 70 Shore A.
14. Shaped article containing a thermoplastic elastomer according to claim 11, characterized in that the compression set (ISO 815) of said article is between 10 and 50%.
15. Shaped article containing a thermoplastic elastomer according to claim 11, characterized in that the compression set (DIN 35517, B) of this article is between 10 and 70%.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 00/00177

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L101/00 C08L21/00 C08L77/00 C08J3/22 C08L67/02
 //(C08L101/00.91:00),(C08L21/00.91:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08J C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | EP 0 659 824 A (HUELS CHEMISCHE WERKE AG) 28 June 1995 (1995-06-28) page 2, line 20 - line 50; claims 1-11 page 3, line 34 - line 36 --- | 11-15 |
| X | US 4 141 863 A (PATEL RAMAN ET AL) 27 February 1979 (1979-02-27) page 1, column 1, line 10 - line 15 page 2, column 4, line 8,9 page 3, column 6, line 10 -page 4, column 7, line 30 page 4, column 9, line 29 -page 4, column 10, line 26; claim 1: tables 2,3 --- -/-- | 11-15 |

☒ Further documents are listed in the continuation of box C

☒ Patent family members are listed in annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

18 May 2000

Date of mailing of the international search report

30/05/2000

Name and mailing address of the ISA

European Patent Office, P B 5818 Patentaan 2
 NL - 2280 HV Rijswijk
 Tel (+31-70) 340-2040, Tx 31 651 epo nl
 Fax: (+31-70) 340-3016

Authorized officer

Bergmans, K

INTERNATIONAL SEARCH REPORT

Int lional Application No
PCT/NL 00/00177

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| Y | EP 0 742 268 A (ADVANCED ELASTOMER SYSTEMS) 13 November 1996 (1996-11-13) page 1, line 51 - line 60 page 2, line 19 -page 3, line 13 page 3, line 51 - line 59; tables 1,2,5 | 1-15 |
| Y | US 3 985 702 A (HIMES GLENN ROY) 12 October 1976 (1976-10-12) page 3, column 3, line 55 - line 65 | 1-15 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 00/00177

| Patent document cited in search report | | Publication date | Patent family member(s) | | Publication date |
|---|---|---------------------|----------------------------|---------------|---------------------|
| EP 0659824 | A | 28-06-1995 | DE | 4343586 A | 22-06-1995 |
| US 4141863 | A | 27-02-1979 | AU | 513348 B | 27-11-1980 |
| | | | AU | 2603177 A | 14-12-1978 |
| | | | BE | 855586 A | 12-12-1977 |
| | | | BR | 7703766 A | 23-05-1978 |
| | | | CA | 1077633 A | 13-05-1980 |
| | | | DE | 2726177 A | 22-12-1977 |
| | | | ES | 459688 A | 01-05-1978 |
| | | | FR | 2354369 A | 06-01-1978 |
| | | | GB | 1533227 A | 22-11-1978 |
| | | | IT | 1077311 B | 04-05-1985 |
| | | | JP | 1103518 C | 16-07-1982 |
| | | | JP | 52152438 A | 17-12-1977 |
| | | | JP | 55014099 B | 14-04-1980 |
| | | | NL | 7706334 A, B. | 13-12-1977 |
| EP 0742268 | A | 13-11-1996 | US | 5574105 A | 12-11-1996 |
| | | | AU | 697634 B | 15-10-1998 |
| | | | AU | 5221696 A | 21-11-1996 |
| | | | BR | 9602206 A | 07-04-1998 |
| | | | CA | 2174908 A | 13-11-1996 |
| | | | CN | 1139686 A | 08-01-1997 |
| | | | JP | 9025370 A | 28-01-1997 |
| US 3985702 | A | 12-10-1976 | NONE | | |